UDC 666.293

CORROSION OF STEEL UNDER ENAMEL COATING

L. G. Protasova,[1] V. G. Kosenko,[1] and E. P. Farafontova[1]

Translated from Steklo i Keramika, No. 7, pp. 31 – 32, July, 2003.

The technological properties of industrial enamel compositions used to coat oil pipes are studied. The characteristics of the process of steel corrosion under a layer of enamel coating are identified, which can be used to optimize the firing process.

The compositions of enamels used for protection of oil pipes have to meet the following requirements: be low-melting (softening temperature 510 – 530°C), wet a metal surface well and spread over it, and have a "long" temperature dependence of viscosity in order to exclude defects known as "fish scale." Firing of enamel coatings should be implemented to form a high-quality coating with high adhesion strength, impact strength, and wear resistance. Strong adhesion of coating to metal in firing is achieved by the formation of an intermediate layer. The higher the rate of corrosion of metal and its dissolution in the enamel melt in firing, the sooner the intermediate layer is formed and the higher the strength of adhesion of enamel to metal.

The study in [1] investigated the corrosion of steel 08kp under a melt of the composition (molar content): $33Na_2O \cdot 67B_2O_3$ depending on partial pressure of oxygen P_{O_2}, which at $P_{O_2} > 100$ HPa is determined by the rate of corrosion of steel and at $P_{O_2} > 250$ HPa by the melt flow under the effect of surface forces. The study in [2] represents metal oxidation curves at a temperature of 800°C under silicate coating of the composition $16Na_2O \cdot 2Me_mO_n \cdot 64SiO_2$ (molar content), where Me_mO_n means PbO, B_2O_3, CdO, Fe_2O_3, ZnO, CaO, MgO, MnO, or CuO. After 30 min of firing, the weight increment reaches 0.5 – 1.5 mg/cm^3, the maximum value observed when Me_mO_n is PbO and B_2O_3.

The purpose of the present study is to investigate the technological properties of enamels and the process of steel corrosion under a coat of industrially produced enamels used to protect oil pipes and to estimate the mechanical properties of the enamel coating.

The surface tension of enamel melts and the wetting angle of metal surface were determined by the lying drop method; the viscosity of melts was measured on a viscosimeter. The corrosion process was studied with a Paulik – Paulik – Erdey derivatograph by the thermogravimetric method. Samples were steel plates of size 10 × 10 mm covered by enamel powder of mass 0.14 – 0.15 g that were placed in the derivatograph furnace and heated at a rate of 8 K/min to a firing temperature of 810 – 820°C. The total duration of the experiment was 1 h. Mass variations were registered on a photographic paper. The impact strength and wear resistance of enamel coatings produced by dry enameling were determined using the standard methods.

Table 1 lists the technological properties of ten enamel compositions. It can be seen that compositions 5, 8, 9, and 10 form a melt drop already at a temperature of 700°C, the first four compositions have relatively low surface tension values (257 – 289 mN/m) and viscosity ($\log \eta = 2,5 – 6.0$) and good spreadability (3 – 24° at 820°C).

Thermogravimetric analysis demonstrated that corrosion of metal proceeds in two stages (Table 2). In the first stage at a temperature of 680 – 810°C the corrosion rate in most enamels is high: $\alpha_1 = 0.420 – 0.900$ mg/(cm^2 · min). This is due to the fact that before the fusion of enamel, oxygen diffuses to the surface of steel and oxidizes it, and consequently scale is formed:

$$2Fe + O_2 = 2FeO;$$

$$2Fe + 2O_2 = Fe_3O_4.$$

In the second stage under a higher temperature (780 – 810°C) the process of corrosion under melted enamel is retarded after the fusion of enamel: $\alpha_2 = 0.030 – 0.267$ mg/(cm^2 · min). Diffusion of oxygen via the enamel coat layer is impeded and iron oxides start dissolving in the melted coating, as a consequence of which a transitional layer is formed. The total mass increment $\Sigma\Delta m$ characterizes the size of the transitional layer and has a direct effect on the mechanical properties of enamel coating.

[1] Ural State Technical University (UPI), Ekaterinburg, Russia.

TABLE 1

Enamel	Wetting angle, deg, at temperature, °C				Viscosity log η at temperature, °C				Surface tension, mN/m at temperature, °C			
	700	750	800	820	700	750	800	820	700	750	800	820
1	No drop	< 10	2	2	3.5	3.0	2.5	1.5	325	258	253	257
2	The same	80	10	3	5.7	5.0	4.5	3.0	287	262	258	259
3	″	< 10	2	2	6.0	5.4	3.8	3.7	365	318	286	289
4	″	No drop	63	24	8.9	7.8	6.0	6.2	285	281	276	271
5	70	47	< 10	3	7.8	6.8	7.8	5.7	≫ 400	400	369	335
6	No drop	> 90	40	21	5.0	3.5	6.6	3.2	> 540	> 540	> 540	> 540
7	The same	No drop	> 90	66	8.8	8.1	8.0	7.5	> 540	> 540	> 540	> 540
8	70	40	< 10	2	10.5	9.8	8.5	10.5	285	276	270	265
9	60	30	16	< 10	7.8	5.8	7.8	4.2	330	302	275	254
10	45	27	< 10	3	7.5	7.2	6.5	6.5	285	273	265	257

TABLE 2

Enamel	τ_1, min	t_1,* °C	α_1, mg/(cm^2 · min)	τ_2, min	α_2, mg/(cm^2 · min)	Δm_2, mg	Δm_1, mg	$\Sigma\Delta m$, mg
1	27	690	0.474	46	0.267	8.0	9.0	17.0
2	25	680	0.200	49	0.120	3.0	6.0	9.0
3	32	780	0.200	79	0.230	3.0	10.0	13.0
4	37	810	0.500	65	0.150	5.0	18.0	23.0
5	24	680	0.110	52	0.030	1.5	3.0	4.5
6	27	700	0.420	44	0.094	3.0	5.0	8.0
7	26	685	0.170	42	0.098	2.9	7.0	7.0
8	35	800	0.690	50	0.210	8.0	9.0	17.0
9	34	800	0.500	52	0.184	7.0	9.0	16.0
10	32	795	0.900	44	0.109	5.0	10.0	15.0

* t_2 in all cases was 820°C.

TABLE 3

Enamel	Spreading stress in enameled steel plate, kg/m^2		Impact strength, J	Wear resistance, m^2/kg
	start of crack formation in coating	coating flaking of metal		
1	19.4	29.1	5.2	2.7
2	19.6	28.9	6.7	2.6
3	22.3	28.0	5.4	1.7
4	26.6	29.8	5.7	2.0
5	18.0	31.7	5.4	1.9
6	23.2	28.6	5.6	2.0
7	26.3	29.2	5.8	2.4
8	25.2	28.5	5.4	2.2
9	31.0	33.6	5.3	2.4
10	21.9	28.1	5.4	2.1

The values τ_1, t_1, α_1, τ_2, t_2, α_2, and $\Sigma\Delta m$ depend on the composition of enamels, which can be split into two groups. Corrosion in the first group starts at lower temperatures, the corrosion rate is not high, and the transitional layer is optimum (Table 3). However, the firing duration for these compositions should be strictly monitored, since after 1 – 1.5 h the enamel melt becomes saturated with iron oxides and electrochemical corrosion starts:

$$Fe - 2\bar{e} = Fe^{2+};$$

$$Fe^{3+} + \bar{e} = Fe^{2+}.$$

Its rate is 10 times higher than α_1, which results in burn-through of the enamel coating.

Thus, the rate of the corrosion of metal under an enamel coating depends both on the melt composition and on the time-temperature characteristics of the firing process.

REFERENCES

1. P. I. Buler and O. R. Lazutkina, "The effect of partial oxygen pressure on the rate of corrosion propagation in steel by means of melted vitreous coating," *Zashchita Metall.*, **22**(5), 84 – 86 (1986).
2. A. L. Appen, *Temperature-Resistant Inorganic Coatings* [in Russian], Khimiya, Leningrad (1976).